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| (54) Title: DETERGENT COMPOSITIONS HAVING A CELLULOSE POLYMER (57) Abstract <p>The present invention relates to a laundry detergent composition comprising an anionically modified cellulose (AMC); and a cationic metal ion. The molar ratio of the anionically modified group of the AMC to the cationic metal ion is preferably from about 50:1 to about 1:50. The laundry detergent composition containing such materials maintain a good fabric appearance, such as better pill/fuzz prevention and color maintenance.</p> | | |

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DETERGENT COMPOSITIONS
HAVING A CELLULOSE POLYMER

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FIELD

15 The present invention relates to a laundry detergent composition containing a cellulose polymer. More specifically, the present invention relates to a laundry detergent composition containing a cationic metal ion and a cellulose polymer.

BACKGROUND

20 Laundry detergent compositions usually contain anionic surfactants and builders. After washing fabric, however, consumers are not always satisfied with the result of the washing. For example, especially on cotton fabric, pill/fuzz on the fabric surface is formed after multiple washings. Pill/fuzz on the fabric surface is not preferable because consumers believe that the fabric has become
25 weak or worn and/or the fabric does not feel soft. In addition, if consumers wash colored fabric, sometimes the fabric color becomes faded. Thus, color maintenance is another important factor for detergent compositions. A detergent composition containing cellulase is known for removing pill/fuzz on the fabric surface. Also detergent compositions containing chlorine scavengers were
30 developed for improving color maintenance. However chlorine scavengers may react with a bleach in a detergent composition easily. Therefore, it is difficult to add chlorine scavengers in detergent compositions containing a bleach because the performance of the bleach may be reduced.

35 There is a continuing need to formulate detergent compositions to reduce the amount of pill/fuzz formed on a washed fabric's surface. In addition, there is

a continuing need to have detergent compositions that have color maintenance properties.

None of the existing art provides all or the advantages and benefits of the present invention.

5

SUMMARY

The present invention relates to a laundry detergent composition containing a mixture of a cationic metal ion and an anionically modified cellulose (AMC). In a preferred laundry detergent composition the molar ratio of the anionically modified group to cationic metal ion is from about 50:1 to about 1:50.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

15

DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed the present invention will be better understood from the following description.

All percentages are by weight of total composition unless specifically stated otherwise.

All ratios are weight ratios unless specifically stated otherwise.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompassed the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

The present invention relates to a laundry detergent composition containing an anionically modified cellulose (AMC) and a cationic metal ion, wherein the molar ratio of the anionically modified group of the AMC to the cationic metal ion is from about 50:1 to about 1:50, preferably, from about 20:1 to about 1:20, and more preferably, from about 10:1 to about 1:10.

The present invention substantially prevents pill/fuzz from forming on the fabric surface after multiple washings. The present invention also provides better

color maintenance over multiple washings. Pill/fuzz is formed on a fabric's surface by many reasons, including for example, by the fabric friction during washing process as well as wearing. Because fabrics contains fibers, after multiple washings, fibers sometimes become unraveled or disentangled. As a result, fibers appear on the fabric surface and form pills. This phenomenon is called pill/fuzz formation.

Although not wanting to be limited by theory, it is believed that when the fabric surface is substantially coated with AMC, pill/fuzz formation is substantially prevented. Both the AMC and the fabric surface, especially cotton fabrics, hold a negative charge. Although the AMC holds a negative charge, the AMC easily attaches to the fabric surface because the structure of the AMC and fabric surface are similar (both have a type of cellulose molecule in their structure). But the physical structure itself is not sufficient to deposit the AMC substantially on the entire fabric surface, so that the pill/fuzz formation is not substantially avoided. Since a cationic metal ion holds a positive charge, a cationic metal ion can neutralize the charge of the AMC. As a result, the addition of a cationic metal ion can help the AMC be deposited more easily on the fabric surface.

Color maintenance is meant to prevent the fabric fading. Although not wanting to be limited by theory, it is believed that if the fabric surface is coated with the AMC, the dye on the fabric surface is prevented from detaching and dissolving into the wash water. Many dye like direct dye hold a negative charge. Although the AMC also has a negative charge, the addition of a cationic metal ion can help the AMC deposit to the fabric surface to substantially prevent the fading of the fabric.

In detergent compositions containing anionic surfactants, if some cationic metal ions are added, it may neutralize the charge of the anionic surfactant in the washing solution because anionic surfactants also hold a negative charge. If the level of cationic metal ion becomes high, the anionic surfactant may not perform well because the anionic surfactant is precipitated by the cationic metal ion. Thus, the addition of AMC with a cationic metal ion in a detergent composition may also prevent a negative affect on anionic surfactant performance.

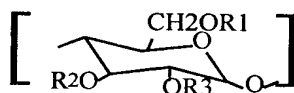
In the present invention, the AMC and the cationic metal ion can be added into the composition separately or, preferably added as a pre-mixture to have more strong interaction between AMC and cationic ions. If a pre-mixture of AMC and cationic metal ion is first made, the AMC and cationic metal ion may have

more strong interaction. It leads to more effective AMC deposition on fabrics and less interaction with other detergent ingredients, such as anionic surfactant.

A fabric substantially coated with AMC may also prevent the redeposition of removed stains onto the fabric from the wash water.

1. Anionically Modified Cellulose

The composition of the present invention contains an anionically modified cellulose (AMC), wherein the cellulose has at least one anionically modified group substitution. A monomer of the cellulose is illustrated below,



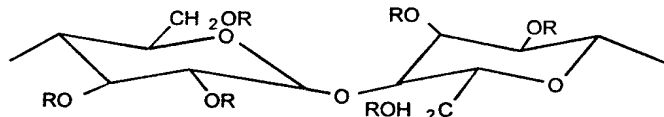
Formula I

wherein $n=10$ to 10000 , preferably, $n=50$ to 5000 , more preferably, $n=100$ to 3000 . At least one of R_1 , R_2 , and R_3 are substituted with an anionically modified group selected from the group consisting of carboxyl, sulphonyl, or phosphonyl group. The remaining R_1 , R_2 and R_3 are substituted from the group consisting of carboxyl, sulphonyl, phosphonyl, acetyl, ether, ester, hydrogen, alkyl, hydroxyl or amido groups.

The degrees of substitution (DS) for Formula I of the anionically modified group is preferably from about 0.2 to about 1.2 , more preferably, from about 0.3 to about 0.7 .

Preferable AMC is selected from the group consisting of ether modified carboxymethyl cellulose, ether modified carboxyethyl cellulose, ether modified carboxymethylethyl cellulose, ester modified carboxymethyl cellulose, ester modified carboxy ethylcellulose, ester modified carboxymethylethyl cellulose, amido modified carboxymethyl cellulose, amido modified carboxyethyl cellulose, amido modified carboxymethylethyl cellulose, and mixtures thereof.

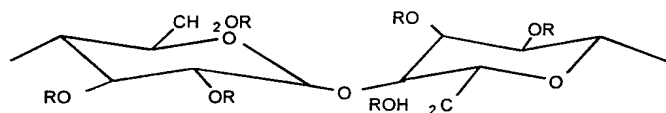
More preferable AMC are shown as the following:



R : $-H$ or $-CH_2COONa$ or $-COCH(C_{1-24}H_{3-49})COCH_2(C_{1-24}H_{3-49})$

DS : $-CH_2COO^- = 0.5$, $-COCH(C_{1-24}H_{3-49})COCH_2(C_{1-24}H_{3-49}) < 0.07$

C12-14 Ester Modified Carboxymethylcellulose



R: -H or -CH₂COONa or -CH₂CH(OH)(C₁₋₂₄H₃₋₄₉)

DS: -CH₂COO⁻ = 0.5, -CH₂CH(OH)(C₁₋₂₄H₃₋₄₉) < 0.07

C12-14 Ether Modified Carboxymethylcellulose

5 The composition of the present invention contains an AMC by weight percent of the total detergent composition, preferably from about 0.1% to about 20%, more preferably, from about 0.5% to about 10%, even more preferably from about 2% to about 5%.

10 Although the AMC can be used in any available physical form, such as a powder form or liquid form, the AMC is preferably in a powder form. The mean particle size of the AMC is preferably from about 5 microns to about 10000 microns, and preferably, from about 80 microns to about 8000 microns. The moisture of a powder form of AMC is preferably from about 3% to about 20%, preferably from about 7% to 13%, by weight of the AMC.

15

2. Cationic Metal Ion

The compositions of the present invention also contain a cationic metal ion. A cationic metal ion means a positively charged metal ion. The cationic metal ion can be added to the present composition in the metal ion form or added in the salt form. A preferred cationic metal ion is selected from the group consisting of alkaline metal ion, alkaline earth metal ion, aluminium, and mixtures thereof. A more preferred cationic metal ion is selected from the group consisting of magnesium, calcium, aluminium, and mixtures thereof. A preferred cationic metal salt is selected from the group consisting of chloride, sulphate, nitrate, succinate, phosphate and mixtures thereof. A more preferred metal salt is selected from the group consisting of chloride, sulphate, nitrate, and mixtures thereof.

25 A preferred cationic metal ion salt is selected from the group consisting of magnesium chloride, magnesium sulphate, magnesium nitrate, calcium chloride, calcium sulphate, calcium nitrate and mixtures thereof.

30 The composition of the present invention contains a cationic metal ion by weight percent of the total detergent composition, preferably from about 0.1% to

about 20%, more preferably, from about 0.25% to about 5%, and even more preferably from about 0.5% to about 3% .

The cationic metal ion may preferably be in any available physical form, such as a powder form or liquid form.

5

ADDITIONAL COMPONENTS

Detersive surfactant

The detergent compositions of the present invention may further include surfactants wherein the surfactant can be selected from the group consisting of
10 nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.01% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accord with
15 the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

20 Preferred surfactants to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

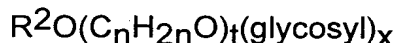
Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the present invention,
25 with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present
30 in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are
35 commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactants of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohol having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KryoTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful nonionic surfactants of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is

attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

5 The preferred alkylpolyglycosides have the formula



10 wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To
15 prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

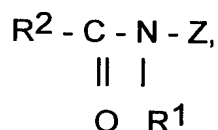
20 The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic deterative surfactant of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water
25 insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide.
30 Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

 Also suitable for use as the nonionic surfactant of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of
35 these products consists of the reaction product of ethylenediamine and excess

propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.



20

wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

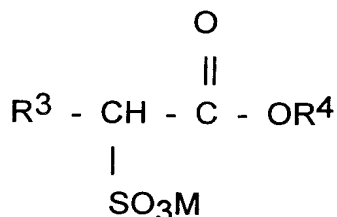
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Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

30

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :

35



wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates,

alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl
5 sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and
10 hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to
15 Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

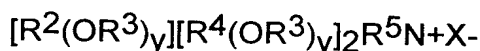
When included therein, the detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

20 Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is
25 greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples
30 of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₈E(1.0)M),
35 C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl

polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)M), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

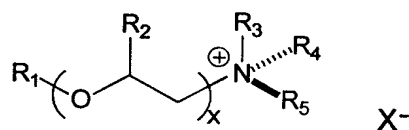
The detergent compositions of the present invention may also contain
 5 cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium
 10 surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



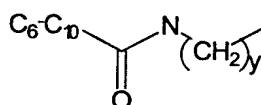
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18
 15 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOH-COR⁶-CHOH-CH₂OH wherein R⁶ is any hexose or hexose
 20 polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

25 Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R₁ is a short chainlength alkyl (C₆-C₁₀) or alkylamidoalkyl of the
 30 formula (II) :



Formula II

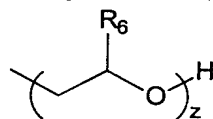
y is 2-4, preferably 3.

whereby R₂ is H or a C₁-C₃ alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

- 5 whereby R₃, R₄ and R₅ are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxyated alkyl of the formula III,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

10 R₆ is C₁-C₄ and z is 1 or 2.

Preferred quaternary ammonium surfactants are those as defined in formula I whereby

- 15 R₁ is C₈, C₁₀ or mixtures thereof, x=0,
R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄₀)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

- 25 The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂R₃ and R₄ are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

- 30 Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;

decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C₁₂₋₁₅ dimethyl hydroxyethyl ammonium chloride or bromide;
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 5 lauryl dimethyl benzyl ammonium chloride or bromide;
 lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
 choline esters (compounds of formula (i) wherein R₁ is
 CH₂-CH₂-O-C-C₁₂₋₁₄ alkyl and R₂R₃R₄ are methyl).



10 di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent
 4,228,044, Cambre, issued October 14, 1980 and in European Patent
 15 Application EP 000,224.

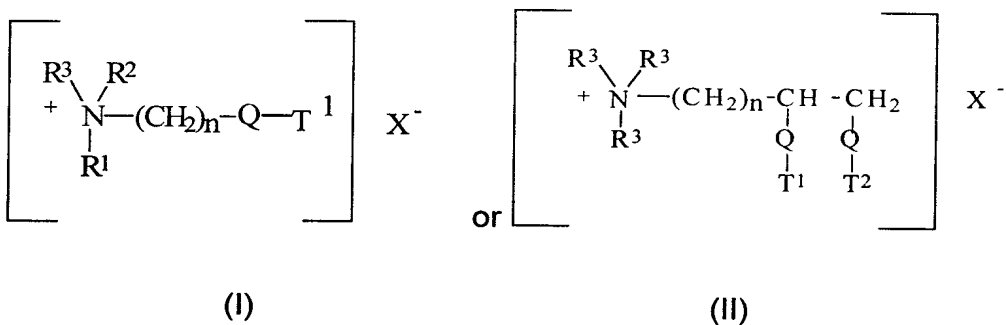
Typical cationic fabric softening components include the water-insoluble
 quaternary-ammonium fabric softening actives or their corresponding amine
 precursor, the most commonly used having been di-long alkyl chain ammonium
 chloride or methyl sulfate.

20 Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 25 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 30 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
- 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 35 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

R¹ is (CH₂)_n-Q-T² or T³;

R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;

R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;

R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;

n and m are integers from 1 to 4; and

X⁻ is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 - 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
 - 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 - 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 - 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
 - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
 - 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

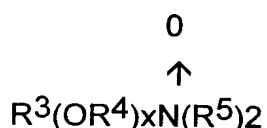
Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or

derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

5 When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety
10 of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from
15 about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants
20 having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof
25 containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups
30 can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

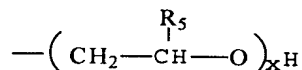
When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may further comprise a
5 cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain or $R_4X(CH_2)_n$, X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be
10 interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n -alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C_8 - C_{10} oxypropylamine, octyloxypropylamine, 2-ethylhexyl-
15 oxypropylamine, lauryl amido propylamine and amido propylamine.

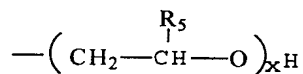
Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R_1 and R_2 are C_1 - C_8 alkylchains or



R_3 is either a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain, or R_3 is $R_4X(CH_2)_n$,
20 whereby X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_4 - C_{12} , n is between 1 to 5, preferably 2-3. R_5 is H or C_1 - C_2 alkyl and x is between 1 to 6.

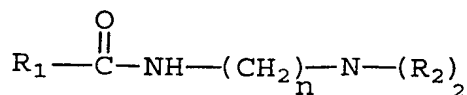
R_3 and R_4 may be linear or branched; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $R_1R_2R_3N$ where R_1 is a C_6 - C_{12} alkyl chain,
25 R_2 and R_3 are C_1 - C_3 alkyl or



where R_5 is H or CH_3 and $x = 1-2$.

30 Also preferred are the amidoamines of the formula:



wherein R₁ is C₆-C₁₂ alkyl; n is 2-4,
preferably n is 3; R₂ and R₃ is C₁-C₄

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl
5 bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine.

10 The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bis(hydroxyethyl)coconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Enzymes

15 The detergent compositions may optionally further contain one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases,
20 phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination is a detergent composition having cocktail of
25 conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are
30 disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and
35 WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-

C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity

throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and
5 MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent
10 Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine
15 at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase
20 variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of
25 +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No.
30 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104,
35 +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170,

+209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed
5 June 04, 1997).

Also suitable for the present invention are protease described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO
10 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is
15 described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention at a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the
20 composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes detergent compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases
25 known for use in detergent compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published
30 August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding

domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills,
5 granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent
10 application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S.
15 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various
20 techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation s are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

25 Color care and fabric care benefits

Technologies which provide a type of color care benefit can optionally also be included in the composition. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in
30 copending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer for color care treatment and perfume substantivity are further examples of color care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent
35 compositions in accordance with the present invention. These agents may be

inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening s include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Bleaching agent

Additional optional detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents.

Preferred peroxygen bleaching agents include those peroxygen bleaching compounds which are capable of yielding hydrogen peroxide in an aqueous solution. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like.

Preferred peroxygen bleaching agents include peroxygen bleach selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof. Specific preferred examples include: sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particular preferred are sodium perborate tetrahydrate, and especially, sodium perborate

monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching solution.

5 These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

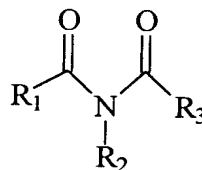
10 The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

15 One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

20 Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

30 The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7

and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



- 5 wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl group.

10 Useful bleaching agents, including peroxyacids and bleaching s comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

15 The hydrogen peroxide may also be present by adding an enzymatic (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic s are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

20 Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the
25 patent application No 94870206.3.

30 Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the

substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

5 Builder

The compositions according to the present invention may further contain a builder. Any conventional builder is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene
10 triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an
15 inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

20 Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic
25 acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives
30 such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates
35 disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates,

1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British
5 Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis -
10 dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

15 Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builders for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.
20 Other preferred builders include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builders for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder for use in granular
25 compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two
30 carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 3% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

Chelating Agents

5 The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that
10 the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

 Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-
15 triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

 Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are
20 permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

 Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to
25 Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

 A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent
4,704,233, November 3, 1987, to Hartman and Perkins.

30 The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

 If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if

utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

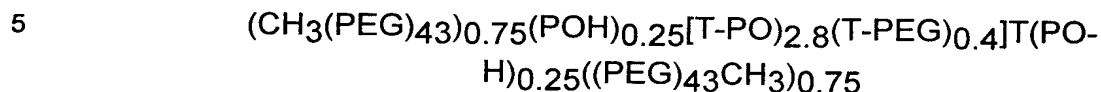
Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4,4'' -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such

polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pcOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise

polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Detergent Composition Preparation

The detergent compositions according to the present invention can be in any physical form, such as a liquid, paste or granular form. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients, e.g., surfactants, builders, water, etc., as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients, e.g., granules of the essential cellulosic based fabric treatment materials, can be admixed in granular powder form with the spray dried granules in a rotary mixing drum. The liquid ingredients, e.g., solutions of the essential cellulosic based fabric treatment materials, enzymes, binders and perfumes, can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Addition of the cellulosic based polymer or oligomer materials to liquid detergent or other

aqueous compositions of this invention may be accomplished by simply mixing into the liquid solutions the desired cellulosic based fabric treatment materials.

EXAMPLES

5

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

10 In the detergent compositions of Example, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions.

Abbreviations used in Examples

15 In the detergent compositions, the abbreviated component identifications have the following meanings:

Amylase: Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T

Brightener 1: Disodium 4,4'-bis(2-sulphostyryl)biphenyl

20 **Carbonate:** Anhydrous sodium carbonate with a particle size between 200µm and 900µm

Cellulase: Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme

CFAA: C₁₂-C₁₄ (coco) alkyl N-methyl glucamide

25 **Citrate:** Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm

Citric acid: Anhydrous citric acid

CxyAS: Sodium C_{1x} - C_{1y} alkyl sulfate

30 **CxyEz:** C_{1x}-C_{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide

CxyEzS: Sodium C_{1x}-C_{1y} alkyl sulfate condensed with z moles of ethylene oxide

DTPMP: Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060

35 **DTPA:** Diethylene triamine pentaacetic acid

EDDS: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.

HEDP: 1,1-hydroxyethane diphosphonic acid

LAS: Sodium linear C₁₁₋₁₃ alkyl benzene sulfonate

5 **Lipase:** Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase

MA/AA: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000

PB4: Sodium perborate tetrahydrate of nominal formula NaBO₂·3H₂O·H₂O₂

10 **Photoactivated:** Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer

Photoactivated: Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer

15 **Protease:** Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase

Protease I: Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.

PVNO: Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000

20 **PVPVI:** Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000

QAS: R₂.N⁺(CH₃)₂(C₂H₄OH) with R₂ = C₁₂ - C₁₄

QAS 1: R₂.N⁺(CH₃)₂(C₂H₄OH) with R₂ = C₈ - C₁₁

25 **QEA:** bis((C₂H₅O)(C₂H₄O)_n)(CH₃) -N⁺-C₆H₁₂-N⁺-(CH₃) bis((C₂H₅O)-(C₂H₄O))_n, wherein n = from 20 to 30

Silicate: Amorphous sodium silicate (SiO₂:Na₂O = 2.0:1)

Silicone antifoam: Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1

30 **SRP 1:** Anionically end capped poly esters

Sulfate: Anhydrous sodium sulfate

TAED: Tetraacetylenediamine

TEPAE: Tetraethylenepentaamine ethoxylate

TPKFA: C₁₂-C₁₄ topped whole cut fatty acids

Zeolite A: Hydrated sodium aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)

- 5 In the following examples all levels are quoted as % by weight of the composition:

Example 1

Granular detergent compositions

| | A | B | C | D | E |
|-------------|------|------|------|------|------|
| LAS | 8.0 | 8.0 | 8.0 | 2.0 | 6.0 |
| TAS | - | 0.5 | - | 0.5 | 1.0 |
| C46(S)AS | 2.0 | 2.5 | - | - | - |
| C25AS | - | - | - | 7.0 | 4.5 |
| C68AS | 2.0 | 5.0 | 7.0 | - | - |
| C25E5 | 10.0 | 10.0 | 3.4 | 10.0 | 4.6 |
| C25E7 | - | - | 1.0 | - | - |
| C25E3S | - | - | - | 2.0 | 5.0 |
| QAS | - | 0.8 | - | - | - |
| QAS (I) | - | - | - | 0.8 | 0.5 |
| Zeolite A | 18.1 | 18.0 | 14.1 | 18.1 | 20.0 |
| Citric acid | - | - | - | 2.5 | - |
| Carbonate | 13.0 | 13.0 | 27.0 | 20.0 | 10.0 |
| Silicate | 1.4 | 1.4 | 3.0 | 0.3 | 0.5 |
| Citrate | - | 1.0 | - | 3.0 | - |

| | | | | | |
|-----------------------------|--------|--------|--------|------|--------|
| MA/AA | 0.3 | 0.3 | 0.3 | 4.0 | 1.0 |
| PB4 | 9.0 | 9.0 | 5.0 | - | - |
| Percarbonate | - | - | - | - | 18.0 |
| TAED | 1.5 | 0.4 | 1.5 | - | 3.9 |
| NAC-OBS | - | 2.0 | 1.0 | - | - |
| DTPMP | 0.25 | 0.25 | 0.25 | 0.25 | - |
| SRP I | - | - | - | 0.2 | - |
| EDDS | - | 0.25 | 0.4 | - | 0.5 |
| CFAA | - | 1.0 | - | 2.0 | - |
| HEDP | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 |
| QEA | - | - | - | 0.2 | - |
| Protease I | - | - | 0.26 | 1.0 | - |
| Protease | 0.26 | 0.26 | - | - | 1.5 |
| Cellulase | 0.3 | - | - | 0.3 | 0.3 |
| Amylase | 0.1 | 0.1 | 0.1 | 0.4 | 0.5 |
| Lipase (1) | 0.3 | - | - | 0.5 | 0.5 |
| Photoactivated bleach (ppm) | 15 ppm | 15 ppm | 15 ppm | - | 20 ppm |

| | | | | | |
|--|---------|---------|---------|---------|---------|
| PVNO/PVPVI | - | - | - | 0.1 | - |
| Brightener 1 | 0.09 | 0.09 | 0.09 | - | 0.09 |
| Perfume | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 |
| Silicone antifoam | 0.5 | 0.5 | 0.5 | - | 0.3 |
| Carboxymethyl cellulose | - | - | 1.0 | - | 1.0 |
| Carboxyethyl cellulose | - | - | 1.0 | - | - |
| Carboxyethylmethyl cellulose | - | - | - | 1.0 | - |
| Ester Modified Carboxymethylcellulose (C12-14) | 3.0 | 3.0 | 1.5 | 2.0 | 2.0 |
| Ether Modified Carboxymethylcellulose (C12-14) | - | - | 1.5 | 2.0 | - |
| MgCl ₂ | 1.5 | - | 2.0 | 2.0 | 10.0 |
| CaCl ₂ | - | 1.5 | 0.5 | 1.0 | - |
| MgSO ₄ | - | - | 0.25 | - | - |
| Mg(NO ₃) ₂ | - | - | 0.25 | - | - |
| Misc/minors to 100% | balance | balance | balance | balance | balance |
| Density in g/litre | 850 | 850 | 850 | 850 | 850 |

Example 2**Liquid detergent compositions**

| | F | G | H | I |
|------------------|----------|----------|----------|----------|
| LAS | 11.5 | 8.8 | - | 3.9 |
| C25E2.5S | - | 3.0 | 18.0 | - |
| C45E2.25S | 11.5 | 3.0 | - | 15.7 |

| | | | | |
|-------------------------|------|------|-----|------|
| C23E9 | - | 2.7 | 1.8 | 2.0 |
| C23E7 | 3.2 | - | - | - |
| CFAA | - | - | 5.2 | - |
| TPKFA | 1.6 | - | 2.0 | 0.5 |
| Citric acid (50%) | 6.5 | 1.2 | 2.5 | 4.4 |
| Calcium formate | 0.1 | 0.06 | 0.1 | - |
| Sodium formate | 0.5 | 0.06 | 0.1 | 0.05 |
| Sodium cumene sulfonate | 4.0 | 1.0 | 3.0 | 1.18 |
| Borate | 0.6 | - | 3.0 | 2.0 |
| Sodium hydroxide | 5.8 | 2.0 | 3.5 | 3.7 |
| Ethanol | 1.75 | 1.0 | 3.6 | 4.2 |
| 1, 2 propanediol | 3.3 | 2.0 | 8.0 | 7.9 |
| Monoethanol amine | 3.0 | 1.5 | 1.3 | 2.5 |
| TEPAE | 1.6 | - | 1.3 | 1.2 |
| Protease | 1.0 | 0.3 | 1.0 | 0.5 |
| Lipase | - | - | 0.1 | - |
| Cellulase | - | - | 0.1 | 0.2 |
| Amylase | - | - | - | 0.1 |
| SRP1 | 0.2 | - | 0.1 | - |
| DTPA | - | - | 0.3 | - |
| PVNO | - | - | 0.3 | - |
| Brightener 1 | 0.2 | 0.07 | 0.1 | - |
| Silicone antifoam | 0.04 | 0.02 | 0.1 | 0.1 |
| Carboxymethyl cellulose | - | - | 0.5 | 1.0 |
| Carboxyethyl cellulose | - | - | 0.5 | - |
| Carboxymethyl cellulose | - | - | 0.5 | - |

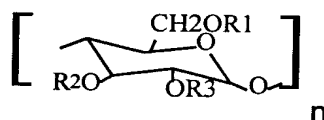
| | | | | |
|--|---------|---------|---------|---------|
| Ester Modified Carboxymethylcellulose (C12-14) | 3.0 | 3.0 | 0.5 | 2.0 |
| Ether Modified Carboxymethylcellulose (C12-14) | - | 2.0 | 1.0 | - |
| MgCl ₂ | 1.0 | 1.0 | 2.0 | 5.0 |
| CaCl ₂ | 0.5 | 1.0 | 3.0 | 2.0 |
| MgSO ₄ | - | 0.5 | - | 1.5 |
| Mg(NO ₃) ₂ | - | 0.5 | - | 1.5 |
| Water/minors to 100% | balance | balance | balance | balance |

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A laundry detergent composition comprising:

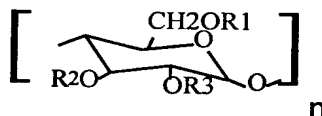
(a) an anionically modified cellulose having the following structure:



wherein $n=10$ to $10,000$; at least one of R_1 , R_2 and R_3 is substituted with an anionically modified group selected from the group consisting of carboxyl, sulphonyl, or phosphonyl group; and

(b) a cationic metal ion, wherein the molar ratio of the anionically modified group to the cationic metal ion is from about 50:1 to about 1:50.

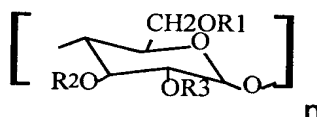
2. A laundry detergent composition according to Claim 1, wherein the AMC has the following structure:



wherein $n=10$ to 10000 ; at least one of R_1 , R_2 , and R_3 is substituted with an anionically modified group selected from the group consisting of carboxyl, sulphonyl, or phosphonyl group and the remaining R_1 , R_2 and R_3 is substituted from the group consisting of carboxyl, sulphonyl, phosphonyl, acetyl, ether, ester, hydrogen, alkyl, hydroxyl or amido groups.

3. The laundry detergent composition according to Claim 2, wherein the AMC is selected from the group consisting of ether modified carboxymethyl cellulose, ether modified carboxyethyl cellulose, ether modified carboxymethylethyl cellulose, ester modified carboxymethyl cellulose, ester modified carboxyethyl cellulose, ester modified carboxymethylethyl cellulose, amido modified carboxymethyl cellulose, amino modified carboxyethyl cellulose, amido modified carboxymethylethyl cellulose and mixtures thereof.

4. The laundry detergent composition according to Claim 1, wherein the cationic metal ion is selected from the group consisting of alkaline metal ion, alkaline earth metal ion, aluminium and mixtures thereof.
5. A laundry detergent composition comprising:
- (a) from about 0.01% to about 60% by weight of a deterative surfactant;
 - (b) from about 3% to about 60% by weight of a detergent builder;
 - (c) from about 0.1% to about 20% by weight of an anionically modified cellulose (AMC) having the following structure:



- wherein $n=10$ to $10,000$; at least one of R_1 , R_2 and R_3 is substituted with an anionically modified group selected from the group consisting of carboxyl, sulphonyl, or phosphonyl group; and
- (d) from about 0.1% to about 20% by weight of a cationic metal ion, wherein the molar ratio of the anionically modified group of the AMC to the cationic metal ion is from about 50:1 to about 1:50.

6. The laundry detergent composition according to Claim 5, wherein the surfactant is selected from the group consisting of anionic, cationic, amphoteric, nonionic, and mixtures thereof; and the detergent builder is selected from the group consisting of pyrophosphates, orthophosphates, tripolyphosphates, higher phosphates, alkali metal carbonates and bicarbonates, alkali silicates, aluminosilicates, polycarboxylates, and mixtures thereof.
7. The laundry detergent composition according to Claim 5, wherein the AMC is selected from the group consisting of ether modified carboxymethyl cellulose, ether modified carboxyethyl cellulose, ether modified carboxymethylethyl cellulose, ester modified carboxymethyl cellulose, ester modified carboxyethyl cellulose, ester modified carboxymethylethyl cellulose, amido modified carboxymethyl cellulose, amino modified carboxyethyl cellulose, amido

modified carboxymethylethyl cellulose and mixtures thereof and the cationic metal ion is selected from the group consisting of alkaline metal ion, alkaline earth metal ion, aluminium and mixtures thereof.

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8. The laundry detergent composition according to Claim 5, further comprising an enzyme selected from the group consisting of protease, amylase, lipase, cellulase, peroxidase, and mixtures thereof.
9. The laundry detergent composition according to Claim 5, wherein the cationic metal ion is magnesium ion or calcium ion and the anionically modified cellulose which is selected from the group consisting of ether modified carboxymethyl cellulose, ether modified carboxyethyl cellulose, ether modified carboxymethylethyl cellulose, ester modified carboxymethyl cellulose, ester modified carboxyethyl cellulose, ester modified carboxymethylethyl cellulose, amido modified carboxymethyl cellulose, amino modified carboxyethyl cellulose, amido modified carboxymethylethyl cellulose and mixtures thereof.
10. The laundry detergent composition according to Claim 8, further comprising a bleaching agent selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof.

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INTERNATIONAL SEARCH REPORT

International Application No

PC 1, US 99/00145

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D3/22 C11D3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | WO 98 29528 A (PROCTER & GAMBLE) 9 July 1998 (1998-07-09) page 8, paragraph 3 - page 9, paragraph 2 page 14, line 6 - page 15, line 3 claims; examples 1,2; table C --- | 1-10 |
| X | EP 0 100 125 A (PROCTER & GAMBLE) 8 February 1984 (1984-02-08) claims 1-9; examples --- | 1,2,4-6, 8 |
| X | DATABASE WPI Section Ch, Week 8239 Derwent Publications Ltd., London, GB; Class A97, AN 82-83057E XP002114949 & SU 883 168 B (CHEM IND RES DES), 23 November 1981 (1981-11-23) abstract --- | 1,2,4-6 |
| -/-- | | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 September 1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/00145

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 2 579 381 A (G.O. FUNDERBURK) 18 December 1951 (1951-12-18) column 2, line 17 - column 3, line 70; claims | 1,2,4 |
| A | ----- US 3 360 470 A (H.E. WIXON) 26 December 1967 (1967-12-26) claims ----- | 1,2,5,6 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JS 99/00145

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|
| WO 9829528 | A | 09-07-1998 | NONE | |
| EP 0100125 | A | 08-02-1984 | AT 39126 T CA 1217107 A DE 3378637 A GR 78636 A IE 55461 B JP 2006230 C JP 7013237 B JP 59085000 A | 15-12-1988 27-01-1987 12-01-1989 27-09-1984 26-09-1990 11-01-1996 15-02-1995 16-05-1984 |
| SU 883168 | B | 23-11-1981 | NONE | |
| US 2579381 | A | 18-12-1951 | NONE | |
| US 3360470 | A | 26-12-1967 | AU 3836563 A BE 643539 A CH 475345 A DE 1469279 A DK 130353 B FR 1390457 A GB 1053388 A NL 6405807 A OA 859 A SE 317763 B | 29-05-1964 15-07-1969 12-12-1968 10-02-1975 16-06-1965 30-11-1964 15-11-1967 24-11-1969 |